Radiocarbon Dating and Salt Production during the Period of Early State Formation on the Tyrrhenian Sea Coast

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Introduction

Radiocarbon dating is the most widely used chronometric technique in archaeology and palaeoenvironmental science. After seven decades of continual refinement, the method is now capable of addressing chronological questions on the generational timescales. This commentary addresses the application of radiocarbon dating to the emergence of the salt industry on the Tyrrhenian Sea littoral. In this specific context, one of the main challenges is the paucity of datable material for either radiocarbon or traditional ceramic-based chronological analysis.

The pivotal role the production and distribution of salt played in the socio-political evolution of early European states is a matter of record, and dealt with extensively elsewhere (Attema 2004; Harding 2013). In the Etruria and Latium Vetus regions, many of the outstanding questions have a chronological dimension. One concerns the local origins of the *briquetage* technique. New data are continually being unearthed, but recent analyses have suggested its time depth stretches well back into the second millennium BCE (Pacciarelli 1991; Alessandri *et al*. 2019). A second issue concerns the local endurance of the *briquetage* technique as the saltern method began to take hold. Whether both methods did co-exist, and what motivated the use of briquetage into the Imperial Period, remains unclear. Finally, dating early salt production processes raises several methodological challenges for radiocarbon-based chronology. Some of these are unique to this specific historical setting, but others have more general implications. An exploration of these issues forms the latter part of this piece.

State of the Art of Radiocarbon Dating

Radiocarbon dating was established in the late 1940s (Libby *et al*. 1949). The method is based on the lifecycle of the eponymous isotope, sometimes denoted ^{14}C. This extremely rare form of carbon is produced continually in the upper atmosphere and, soon after, oxidised to $^{14}CO_2$. Some of the resultant $^{14}CO_2$ enters the biosphere via photosynthesis, which allows the radioisotope to be transmitted up the food chain. Constant replenishment by living organisms means the radiocarbon concentration of their tissues remains in approximate equilibrium with the local atmosphere. However, once this physiological exchange ceases, the amount present in the tissue decays away with a half-life of approximately 5700 years (Kutschera 2019). Thus, by measuring the proportion of radiocarbon in a bio-organic material, an estimate can be obtained of the time elapsed since the antecedent organism was alive. In the late 20th century, it became clear that absolute dates (on the CE/BCE timescale) could only be obtained by correcting radiocarbon measurements against a 'calibration' curve (Stuiver & Pearson 1986; Bronk Ramsey *et al*.

2006). Such reference records are primarily built of radiocarbon measurements on tree-rings whose age has been independently established through dendrochronology. Calibration curves for the Northern and Southern Hemispheres, and for terrestrial and marine samples, have now been produced. The latest versions for the Northern Hemisphere are IntCal20 and Marine20 (Reimer *et al*. 2020). Even though these datasets are constantly being improved and enhanced, the intrinsic presence of 'plateaux' in the curves mean samples measured to the same level of analytical precision generate a wide variety of dating precisions, depending on the period they come from (see Figure 1).

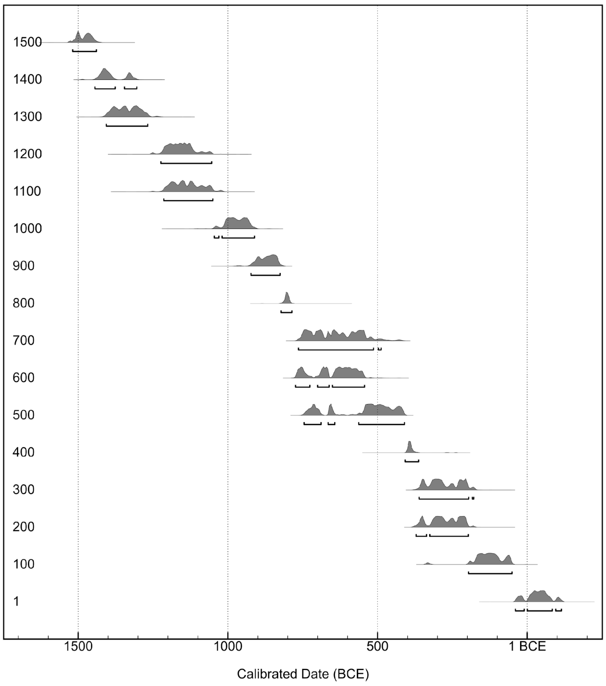

Fig. 1. Simulations of radiocarbon dates for different calendar years (BCE, vertical axis). Each result makes use of the same measurement error (± 20 yr BP), which is a typical value for the Bronze and Iron Ages. It can clearly be seen that some centuries generate much wider absolute date ranges (square brackets beneath distributions, 95% probability) than others.

Over the last 50 years, in effort to combat imprecision in radiocarbon dating, three important developments have taken place. First was the development of radiocarbon measurement by accelerator mass spectrometry (AMS). AMS is capable of obtaining the same level of precision as its forerunning decay-counting methods on samples a thousand times smaller in size. As a result, direct analysis of items such as individual seeds and locks of hair can now be carried out without causing wanton destruction to precious archaeological materials (Bayliss 2009). Presently, AMS analysis of samples from the Bronze and Iron Ages can be routinely obtained with a measurement precision (before calibration) of around ± 20 yrs BP (1σ). However, calibrating such results still tends to result in a date range of more than one century at 95% probability (Figure 1). Fortunately, a second important enhancement, which acts directly on the absolute date ranges, emerged with the development of high-powered computing. Bayesian statistical modelling requires advanced sampling algorithms, and so its use has only become possible over recent decades (Bronk Ramsey 2009). This statistical paradigm enables chronological relationships, established by means such as archaeological stratigraphy, to be brought to bear on groups of radiocarbon results, thereby honing their absolute dating precision (Bronk Ramsey 2009). Some Bayesian modelling studies, where substantial amounts of independent chronological evidence is available, have managed to generate calibrated date ranges of around 20 calendar years for single events, at 95% probability. Many of these studies have centred on the Bronze Age of the Mediterranean region (Manning *et al*. 2006; Bronk Ramsey *et al*. 2010; Dee *et al*. 2013). Finally, within the last 5 years or so a new dimension to radiocarbon dating has emerged. It has been discovered that approximately once a millennium, annual spikes have occurred in the atmospheric concentration of radiocarbon (Miyake *et al*. 2012). These ephemeral surges in radiocarbon production, or Miyake Events, can be used to anchor sequences of radiocarbon determinations and, in certain circumstances, generate calibrated radiocarbon dates that are correct to the exact calendar year (Kuitems *et al*. 2019; Kuitems *et al*. 2021). It is important to note, in the context of the salt production process, that one such spike occurred in the year 660 BCE (Park *et al*. 2020).

The Emergence of Briquetage on the Tyrrhenian Coast

The *briquetage* method of salt extraction first appeared in southeast Europe in the Chacolithic Period (Weller & Dumitroaia 2005; Sordoillet *et al*. 2018). During the Iron Age and Roman Period, the technique spread throughout Europe (Alessandri *et al*. 2019). The timing of its arrival on the Italian peninsula, however, remains unclear. The issue is both one of chronology and of site verification. Some of the earliest claimed *briquetage* sites date to the Bronze Age (*ca*. 2nd millennium BCE), but they are generally characterised by incomplete or ambiguous artefactual assemblages. The details of the ceramic repertoire necessary for an attribution to *briquetage* are beyond the scope of this work but it suffices to say that the diagnostic evidence is not yet universally agreed (Alessandri *et al*. 2019). Reddish jars and kilns are commonly found at the sites, putatively acquiring this colouring from their secondary firing during the salt-process *chaine d'operatoire* (Alessandri *et al*. 2019). However, other factors, such as the underrepresentation of the so-called pedestals upon which the vessels of brine sat, as well as the morphology and chemistry of the ceramics themselves, has made assigning sites to the *briquetage* process extremely difficult (Pacciarelli 1991; Alessandri *et al*. 2019). As a result, alternative explanations, such as locations for fish processing, have been proposed (Belardelli & Pascucci 1998). In order to crystallise the true origins of salt production *per se* on the Italian Peninsula, an archaeological consensus will therefore need to be reached before the corresponding absolute dates can be assigned.

The Overlap between the Briquetage and Saltern Methods

In addition to the origin of *briquetage*, the question of how and when this technique was superseded by the saltern approach also remains unresolved. Salterns comprise a series of shallow pools of brine within which the sodium chloride precipitates via natural evaporation (see Castro-Nogueira *et al*. 1997). With large surface areas, the pools ultimately proved a more efficient method of extraction (Alessandri & Attema 2022). Reliable dates for late *briquetage* and early saltern sites are scarce. Radiocarbon dates for the *briquetage* site of Pelliccione place it within the Late Bronze Age (Attema 2004). Results for the *briquetage* site of Puntone Campo da Gioco similarly situate it in the Final Bronze to Early Iron Ages (1107–841 BCE, Sevink *et al*. 2021). In this case, however, later periods could not be dated by either radiocarbon or traditional typological analysis, in both cases due to a lack of datable samples. The earliest dated salterns in Etruria and Latium Vetus come from the mid 1st millennium BCE (Alessandri & Attema 2022). Taking this and related evidence into account, it is postulated that the more ancient technique of *briquetage* became too cumbersome to meet demand as populations grew and the first polities emerged. However, the correlation between the growth of the saltern process and the emergence of the Early States is one of the questions for which improved chronology is required. Furthermore, the longevity of the *briquetage* technique is itself still an open question. It is not known how abruptly or comprehensively the saltern method took hold. Indeed, some evidence suggests the *briquetage* technique continued to be used for many centuries after saltern sites were commonplace (Alessandri *et al*. 2021).

In the absence of sufficient sherds for typological chronology at many of the sites, the only means by which the question of method overlap, and indeed purpose, can be elucidated is through cutting-edge chronometric methods. This would likely entail the combination of stratigraphy and radiocarbon data within a Bayesian statistical framework. Even then, a significant challenge will be posed by the Halstatt Plateau (~ 750–400 BCE), in the radiocarbon calibration curve (see Figure 1). Thermoluminescence results may also be incorporated in such analyses, but in actuality such data is likely to be too imprecise to make a real difference. Moreover, because well-associated radiocarbon samples are so difficult to find, in order to resolve the matter categorically, attempts may have to involve novel sample types.

Early Salt Production and New Frontiers in Radiocarbon Chronology
Due to a paucity of plant remains at the *briquetage* site at Puntone, a whole host of carbonate samples were analysed (Sevink *et al*. 2020). Carbonates originating from topsoil runoff (pedogenic) and the pre-existing geology (lithogenic) were immediately disregarded. Efforts at isolating secondary carbonates from the salt extraction process itself, as well as directly dating shell material, achieved mixed results. However, certain organic fractions of the sediment did produce credible dates. In the article, Sevink *et al*. (2020) argue that in environments such as discarded *briquetage* pits labile organic matter (LOM), mostly of microbial origin, can become 'fossilised' in sediment, where it would normally be decomposed. At Puntone, the LOM samples returned dates consistent with associated charcoal material, and suggested *briquetage* process continued well into the era of the Roman Republic. This material is subsequently being seen as a potentially valuable sample type at other such sites.

A final aspect to the dating of salt-production sites concerns the relationship between highly saline solutions and the radiocarbon age of the organisms they contain. All marine (saltwater) organisms are offset to older ages compared with contemporaneous terrestrial organisms because the radiocarbon concentration of the ocean is considerably lower than the atmosphere. This is referred to as the marine reservoir effect (see Reimer *et al*. 2020). However, it has never been determined to what extent water salinity exacerbates this effect. In the laboratory, it has been conclusively shown that the solubility of CO_2 is anticorrelated with water salinity (Stewart & Munjal 1970). Thus, conceptually, it is likely that highly saline lagoons, and even more enriched *briquetage* pits and saltern pools, repel atmospheric CO_2 to the point that organisms growing in such environments are extremely offset in their radiocarbon ages. As yet unpublished experimental evidence from the Puntone area seem to support evidence from other highly saline waters (Southon *et al*. 2002; Felis *et al*. 2004), that these environments do give rise to amplified reservoir offsets; however, far more data is required to confirm this trend. Research into this effect will not only aid in the dating of salt production sites, but also make a fundamental contribution to the application of the radiocarbon dating technique.

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